Analytical Study on the Interface of Polymer Blends from Advanced COPNA-Resin and Nylon 6

KAZUNARI NAWA,[1] HIROKO KANATA[2]

[1]R & D Center, Sumitomo Metal Industries, Ltd., 1-8 Fusocho, Amagasaki City, Hyogo 660, Japan
[2]Sumitomo Metals Technology, Ltd., 1-8 Fusocho, Amagasaki City, Hyogo 660, Japan

ABSTRACT: In the previous work, we introduced new polymer blends from the advanced COPNA-resin and nylon 6.[1] The morphology of the polymer blends were quite different between the B-staged state and the fully cured state. In order to investigate a phenomenon occurred in the curing process, ^{13}C Fourier transform–nuclear magnetic resonance (FT-NMR) spectral analysis, ^{15}N FT-NMR spectral analysis, and Fourier transform infrared absorptional spectral analysis were carried out on the blends in a solid state. From the spectral analyses, it was revealed that a graft reaction occurred at the interface between the advanced COPNA-resin and the nylon 6. The difference of the morphology on the fully cured polymer blends was due to the following reason. In the curing process, generated benzyl-type cations of the B-staged Advanced COPNA-Resin initially attacked and combined with nitrogen in the amino groups of the nylon 6. In the late stage of the curing process, the cations mainly attacked and combined with π electrons of the condensed aromatics. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 549–557, 1997

Key words: advanced COPNA-resin; nylon 6; polymer blend; morphological analysis; graft reaction

INTRODUCTION

In order to spread Advanced COPNA-Resin to the materials of electrical insulators, we have embarked on studying the application of the Advanced COPNA-Resin to the flexible film for printed wiring boards. We have already reported fabrication and properties of the novel polymer blend system from the Advanced COPNA-Resin and nylon 6.[1] In the previous work, the system was introduced mainly in order to give sufficient flexibility to the Advanced COPNA-Resin as films for flexible printed wiring boards. Here, we reintroduce the results of the previous work[1] in order to give sufficient background for this new work: the former deals with the properties of the fully-cured polymer blend systems; the latter deals with the morphology of the blends. Table I shows the properties of the polymer blend systems whose fractions are 30/70, 50/50, and 70/30 (COPNA/Nylon 6). The properties of the homopolymer of the Advanced COPNA-Resin and the nylon 6 are also shown in Table I. Characteristic properties of the blends, which are different from the homopolymer of the Advanced COPNA-Resin or the nylon 6, are as follows.

1. The blends exhibited thermosetting property. They exhibited B-staged state when they were removed from the petri dishes.
2. Sufficient flexibility for the flexible films was observed in both the 30/70 and 50/50 (COPNA/nylon 6) systems.
3. The glass transition temperature of the fully-cured blend films was between 153

Table I Properties of the Homopolymer and Fully Cured Polymer Blends From the Advanced COPNA-Resin and the Nylon 6

| System (COPNA/Nylon 6)	0/100	30/70	50/50	70/30	100/0
Film Thickness (μm)	—	65	60	57	—
Flexibility[a]	No cracks	No cracks	No cracks	Cracks	Cracks
Glass transition temperature (°C)	$60 \sim 70$	153	158	168	250
Melting point (°C)	$215 \sim 225$	—	—	—	—
Thermal expansion coefficient (ppm)	80	148	98	69	56
10% weight loss temperature (°C)	—	378	360	380	450
Tensile strength (Kgf/mm^2)	4.0	3.1	3.2	2.8	4.7
Young's modulus (Kgf/mm^2)	—	74	79	83	—
Elongation (%)	200	23	23	29	—
Dielectric constant (1 MHz)	4.5	3.7	3.6	3.5	3.1
Dissipation factor (1 MHz)	0.12	0.01	0.01	0.01	0.003
Volume resistivity (Ωcm)	5×10^{15}	5×10^{15}	3×10^{15}	5×10^{15}	5×10^{15}
Water absorption (wt %)	1.8	3.3	1.4	0.71	0.37

[a] Evaluated by a folding test up to 180 degrees.

and 168°C, which was higher than that of the nylon 6 and lower than that of the Advanced COPNA-Resin.

4. The dielectric constant of the blends was between 3.5 and 3.7, which was higher than that of the Advanced COPNA-Resin and lower than that of the nylon 6.

Figures 1 and 2 show transmission electron microscopy (TEM) images of the B-staged polymer blends and fully-cured polymer blends referred to in the previous work, respectively.[1] In the TEM analysis of the B-staged blend films (Fig. 1), the morphologies were similar to each other in entire systems. The spherulites owing to the phase-separated phenomenon were observed in entire systems. The diameter of the spherulites at the fractions of both 30/70 and 50/50 (COPNA/nylon 6) were approximately 10 μm, and that of 70/30 system was $2 \sim 3$ μm. In the case of the fully-cured systems, the morphology was quite different from the B-staged state. In the TEM analysis of the fully-cured systems (Fig. 2), a phase-separated state, mainly owing to the crystallization of the nylon 6, was observed in entire systems. A typical sea island structure was observed in both the 30/70 and 50/50 (COPNA/nylon 6) systems. The domain size of the Advanced COPNA-Resin was from 0.1 to 2 μm in both systems. From the morphological analysis and flexibility properties, it was proven that those two systems did not exhibit sufficient miscibility but did exhibit sufficient

compatibility for practical uses. The flexibility of both the systems shown in Table I might depend on the morphology shown in Figure 2. In the case of the 70/30 system, it exhibited too poor a compatibility to exhibit sufficient flexibility. From those morphological analyses, it is quite important to discuss a phenomenon occurring in the curing process from the B-staged state to the fully-cured state.

In the historical studies of the polymer blends, the blend systems from entirely thermoplastic resins have been mainly studied,[2–4] while the systems from thermosetting resin/thermoplastic resin[5,6] or entirely thermosetting resins[7] have rarely been studied. From this historical point of view, the new system of COPNA/Nylon 6 might gather interests because the polymer blends consists of a thermosetting resin and a thermoplastic resin. The Advanced COPNA-Resin/nylon 6 system was selected because of good miscibility between Advanced COPNA-Resin and amino groups.[8] Therefore, attention has been focusing on the phenomenon occurring at the interface between the Advanced COPNA-Resin and the nylon 6. In order to analyze the interfacial state, ^{13}C and [15]N Fourier transform−nuclear magnetic resonance (FT-NMR) spectral analyses were carried out in the blends. Fourier transform infrared (FT-IR) absorptional spectral analysis was also carried out in the study. In this report, the analytical study on the interface is mentioned, and the chemical reaction generated at the interface is also discussed.
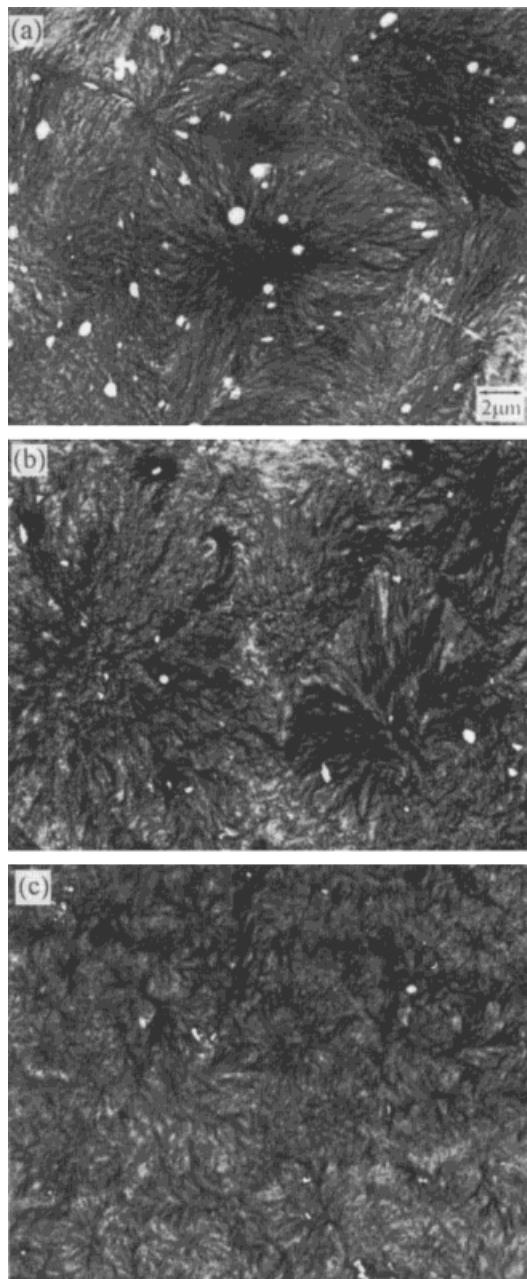
Figure 1 TEM images of the B-staged polymer blends: (a) 30/70, (b) 50/50, and (c) 70/30 (COPNA/ Nylon 6).

EXPERIMENTAL

Samples

Advanced COPNA-Resin was from Sumikin Chemicals (SKR-NM). The molecular weight of the B-staged resin was $M_n = 2.5 \times 10^2$, $M_w = 9.1 \times 10^2$, and $M_w/M_n = 3.70$. Nylon 6 was from Ube Chemicals

(1013B). The molecular weight of the resin is $M_n = 2.82 \times 10^4$, $M_w = 5.59 \times 10^4$, and $M_w/M_n = 1.98$. The properties of the fully-cured Advanced COPNA-Resin and the nylon 6 are already shown in Table I.

Apparatus and Measuring Conditions

FT-NMR Spectral Analysis

The FT-NMR spectral analysis was carried out on solid samples of the fully-cured polymer blends. In
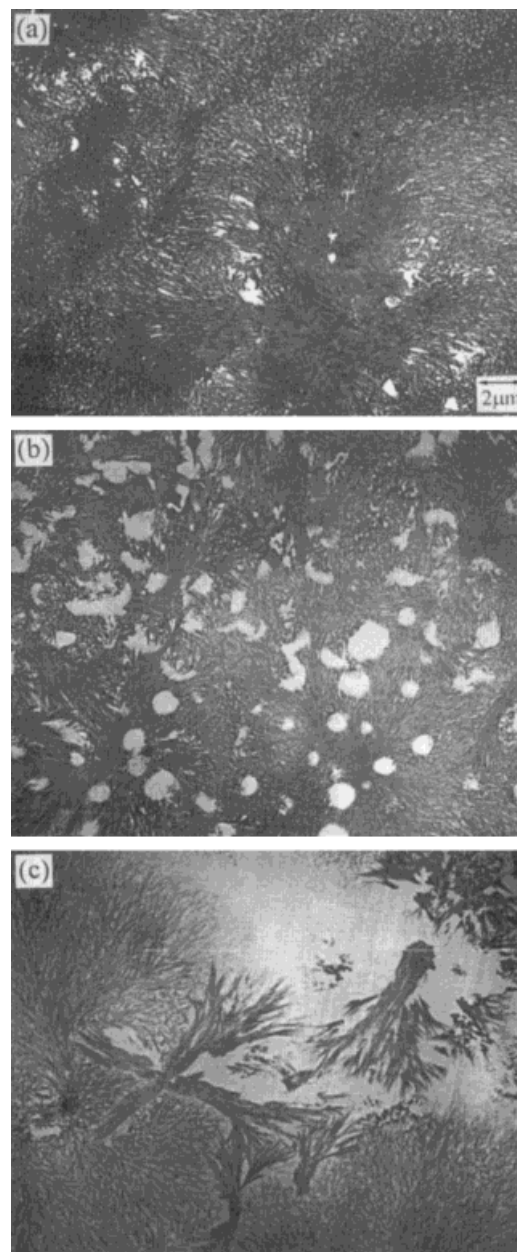
Figure 2 TEM images of the fully-cured polymer blends: (a) 30/70, (b) 50/50, and (c) 70/30 (COPNA/ Nylon 6).

this study, both ^{13}C and ^{15}N FT-NMR spectral analyses were carried out on the fully-cured blends in a solid state. The 240 MHz NMR spectral analyzer was a Nippon Denshi JMN-EX270W, whose probe was from Doty-scientific CPMAS. The spectral analysis was carried out according to the TOSS method, and measuring frequency was 4 KHz. The chemical shift was decided as NH$_4$Cl peak to be the criterion.

FT-IR Spectral Analysis

The FT-IR spectral analysis was carried out by a solid KBr method. The FT-IR spectral analyzer was a Perkin Elmer System 2000. The total count number was 100.

Preparation for the Samples

The samples used in this work were prepared by the film casting method. 9.1 wt % dichloromethane solution of the Advanced COPNA-Resin and 5.4 wt % 1,1,1,3,3,3-hexafluoro-2-propanol solution of the nylon 6 were prepared. Both solutions were mixed at the fractional ratio of 30/70, 50/50, and 70/30 (weight percent of COPNA/Nylon 6). The mixture was cast onto a Petri-dish and was removed from it. The films obtained were dried until the weight did not change. After that process, B-staged polymer blend films were obtained. Fully-cured films were obtained by hot-press fabrication of the B-staged films. The hot-press condition was 180°C/30 min + 230°C/60 min in air. The pressure was 25 Kgf/cm^2. The film thickness of the films obtained was in the range from 50 to 70 μm.

RESULTS

^{13}C FT-NMR Spectral Analysis

Figure 3 shows spectra of ^{13}C FT-NMR of the fully-cured polymer blend films, whose fractions are 30/70, 50/50, and 70/30 (COPNA/Nylon 6), respectively. Spectra of homopolymer of the nylon 6 and the Advanced COPNA-Resin are given for comparison. When the fraction of the nylon 6 decreased, several characteristics were observed in the blend systems.

1. Intensity of the peak inherent in the nylon 6 decreased, and the peak did not exhibit any shift. The inherent peak of carbon in methylene groups was observed at the fre-
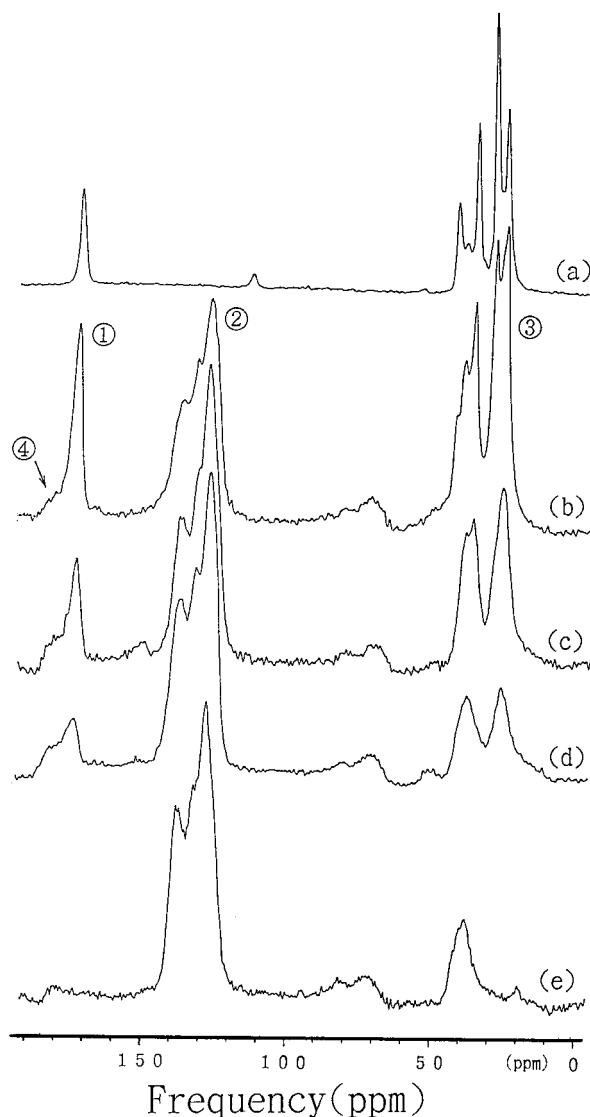
Figure 3 ^{13}C FT-NMR spectra of the blends: (a) 0/100, (b) 30/70, (c) 50/50, (d) 70/30, and (e) 100/0 (COPNA/Nylon 6).

quency of 22 to 32 ppm (peak 3), and that of carbon in carbonyl groups was observed at 174 ppm (peak 1).

2. Intensity of the peak characteristic of the Advanced COPNA-Resin increased, and the peak did not exhibit any shift. The inherent peak of carbon in aromatic groups was observed at the frequency of 120 to 142 ppm (peak 2).

3. A weak peak 4 was newly observed at a higher frequency band than the 174 ppm peak of carbon in carbonyl groups. The peak intensity of the new peak increased

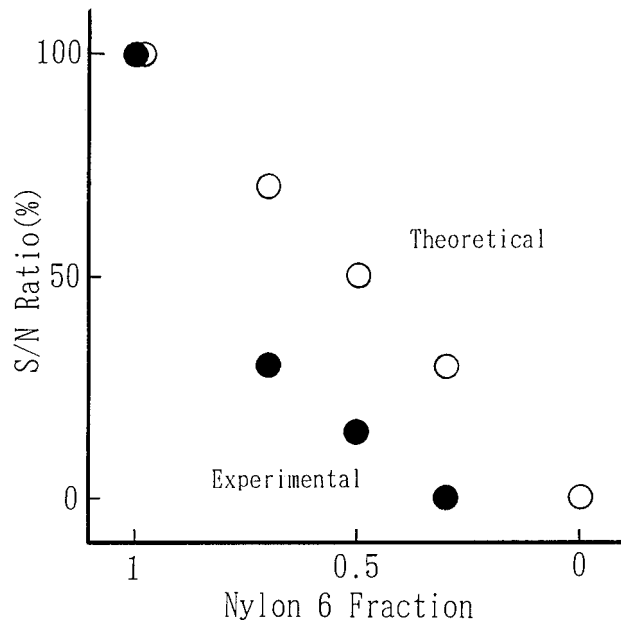according to the decrease of the fraction of nylon 6.

From those three characteristics, it was revealed that the basic structure of both Advanced COPNA-Resin and nylon 6 did not change, while a defined chemical reaction occurred only in the amide combination of the nylon 6 in the blends. The degree of the chemical reaction increased according to the decrease of the nylon 6 fraction.

^{15}N FT-NMR Spectral Analysis

Figure 4 shows ^{15}N FT-NMR spectra of the fully-cured polymer blend films. The spectrum of the nylon 6 homopolymer is also given for comparison. In this analysis, the peak observed at the frequency of −341.17 ppm due to NH$_4$Cl was chosen as a peak reference. In the case of the spectral analysis of amino-groups by the ^{15}N FT-NMR CP/MAS method, it has been known that the peak of nitrogen included in the primary and the secondary amino-groups could be observed, while the peak of the tertiary amino-groups could hardly be observed.[9,10] In the case of the nylon 6 homopolymer, the peak of nitrogen of the secondary amino-groups was observed at the frequency of −262 ppm. The peak intensity of the −262 ppm peak
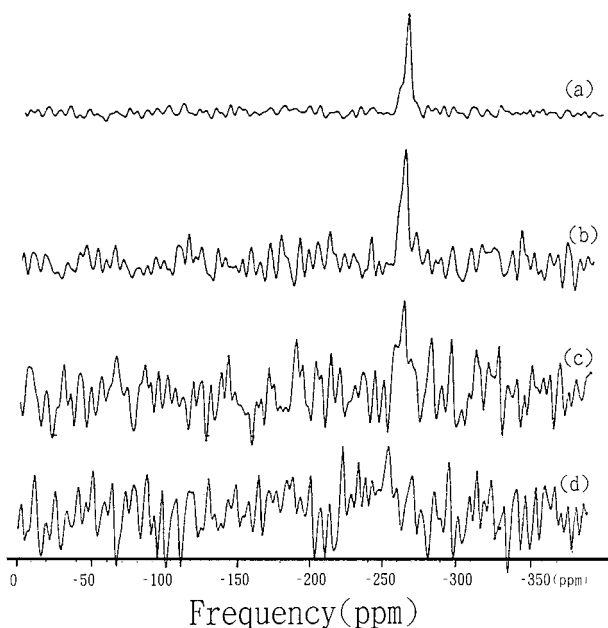
Figure 4 ^{15}N FT-NMR spectra of the blends: (a) 0/100, (b) 30/70, (c) 50/50, and (d) 70/30 (COPNA/Nylon 6).

Figure 5 Dependence of the S/N ratio on the nylon 6 fraction.

decreased according to the decrease of the nylon fraction. The peak of the secondary amino-groups disappeared in the 70/30 (COPNA/Nylon 6) system, although 30 wt % of nylon 6 was included in the system. Figure 5 shows dependence of the signal to noise ratio (S/N ratio) of the secondary amino-groups signal on nylon 6 fraction. In Figure 5, both experimental S/N ratios and theoretical S/N ratios of the signal were plotted. The experimental S/N ratios were converted into relative values where the S/N ratio of the nylon 6 homopolymer system was set at 100. The theoretical S/N ratios were calculated according to the following equation:

[Theoretical S/N ratio]

$$= 100 \times [\text{Nylon 6 fraction}]$$

In Figure 5, the experimental values were smaller than the calculated ones in the blend systems. Therefore, it was supposed that secondary amino-groups of the nylon 6 were partially consumed by the chemical reaction at the interface between the Advanced COPNA-Resin and the nylon 6.

FT-IR Spectral Analysis

In order to get more detailed information of the amino-groups included in the nylon 6, spectral
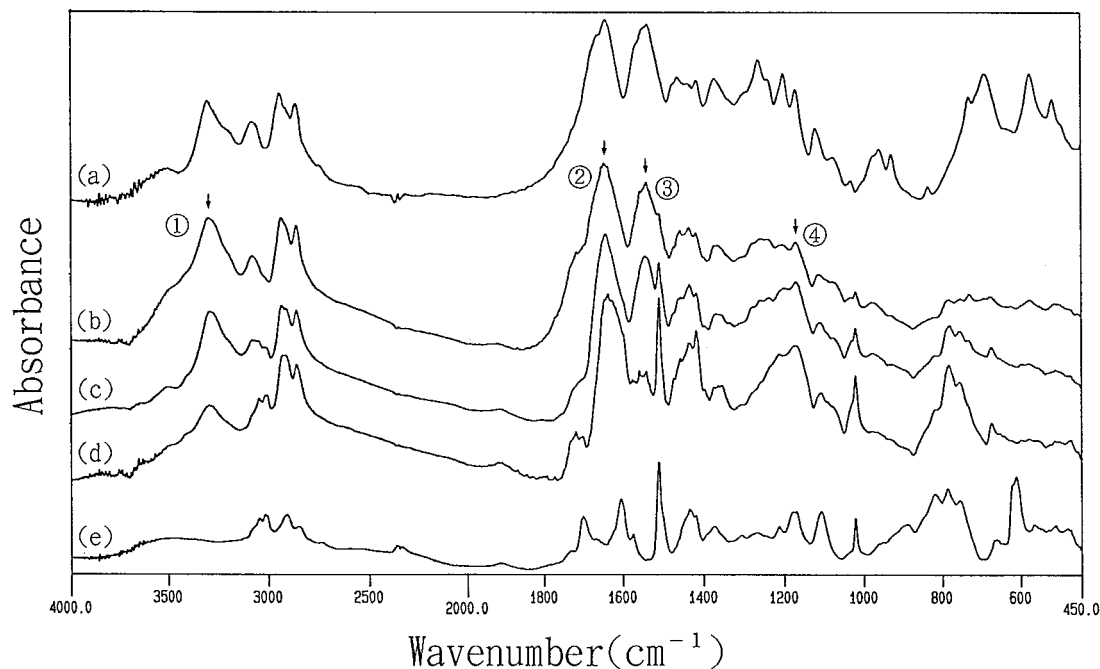
Figure 6 FT-IR spectra of the blends: (a) 0/100, (b) 30/70, (c) 50/50, (d) 70/30, and (e) 100/0 (COPNA/Nylon 6).

analysis for the functional groups of the blends was carried out by the FT-IR absorption spectral analysis method (Fig. 6). The spectra of the homopolymer of the Advanced COPNA-Resin and the nylon 6 are given for comparison. The vertical line indicates absorbance.

The absorption due to the stretching vibration of the C=O combination in amide groups observed at 1635 cm^{-1} (absorption 2) was chosen as an absorption reference; therefore, the absorbance due to the C=O stretching vibration of entire systems was converted in order to exhibit the same value. In this spectral analysis, the following characteristics were revealed when the fraction of the nylon 6 decreased.

1. Both the absorbance observed at 3300 cm^{-1} due to the N—H stretching vibration (absorption 1) and the absorbance observed at 1545 cm^{-1} due to N—H out-of-plane vibration (absorption 3) decreased.
2. The absorbance observed at 1170 cm^{-1} due to the C—N stretching vibration (absorption 4) increased.

From the results of the FT-IR absorption spectral analysis, it was suggested that a defined chemical reaction occurred on the amino-groups of the ny-

lon 6 and that a C—N combination was generated on the amino-groups.

DISCUSSION

Analysis of the Interface Between Advanced COPNA-Resin and Nylon 6

The analytical results studied in this work are summarized as follows.

1. For the ^{13}C FT-NMR spectral analysis, a new chemical combination in the amide group of the nylon 6 was suggested. The new peak was observed at a higher frequency band than the peak of the carbon in the carbonyl group. The degree of the chemical reaction increased according to the decrease of the nylon 6 fraction.
2. For the ^{15}N FT-NMR spectral analysis, secondary amino-groups of the nylon 6 were considered to be partially consumed in the blend systems. Experimental S/N ratios due to the secondary amino-groups were smaller than the calculated ones.
3. For the FT-IR spectral analysis, a new C—N combination in the amino group was
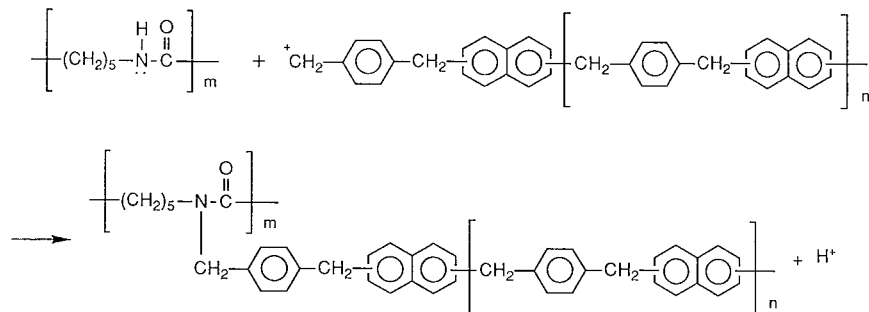
Figure 7 Mechanism of the graft reaction.

suggested. The absorbance of the N—H stretching vibration and the N—H out-of-plane vibration decreased, and the absorbance of the C—N stretching vibration increased, when the fraction of the nylon 6 decreased.

From the results of those spectral analyses, it was suggested that such a graft reaction, as shown in Figure 7, occurred at the interface between the Advanced COPNA-Resin and the nylon 6. The mechanism of the graft reaction will be discussed in the next section. The degree of the graft reaction could be calculated from the absorbance ratio of N—H out-of-plane vibration/C=O stretching vibration. Table II shows the degree of the graft reaction of the blends calculated from the absorbance ratio. The degree of the graft reaction increased when the nylon 6 fraction decreased. The degree of the 30/70 system was only 7.5%, while the degree of the 70/30 system was as large as 82%.

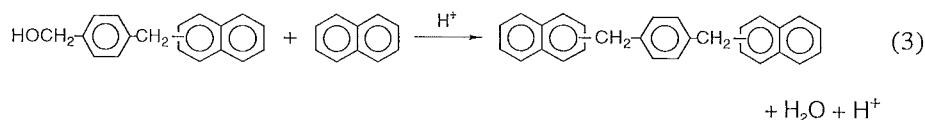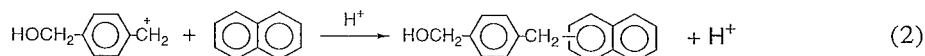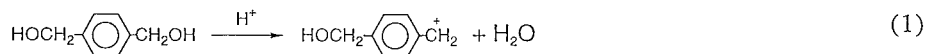### Relationship Between Morphology and the Nylon 6 Fraction

In this section, the relationship between the morphology as shown in Figure 2, and the nylon 6 fraction will be discussed. The mechanism of the graft reaction, as shown in Figure 7, will be also

Table II Degree of the Graft Reaction

System (COPNA/Nylon 6)	Degree of Graft Reaction (%)
30/70	7.5
50/50	42
70/30	82

discussed. The morphologies of the B-staged films were similar to each other in entire systems, as shown in Figure 1, while the morphologies of the fully-cured films were quite different from each other (Fig. 2). Therefore, it is quite important to discuss the phenomenon occurring in the curing process from the B-stage to the fully-cured stage in the blends. In order to give sufficient background for this section, the reaction mechanism of the Advanced COPNA-Resin referred to in the previous work[11] is given in Figure 8. The reaction of the Advanced COPNA-Resin was proceeded by the electrophilic reaction. Primary benzyl-type cations were generated under the acid catalyst in the system (eq. 1 of Fig. 8). Secondly, the generated benzyl-type cations attacked and combined with the π-conjugated condensed aromatics, such as naphthalene (eq. 2 of Fig. 8). According to the repeat of both the processes, as shown in Figure 8 (eq. 1 and 2), molecular weight of the Advanced COPNA-Resin increased (eq. 3 of Figure 8) and, finally, B-staged Advanced COPNA-resin, whose M_n was 2.5×10^2, was obtained. In the B-staged Advanced COPNA-Resin, not only benzyl-type cations, whose molecular weight was comparatively small, but also nonreacted naphthalene and aromatics also existed because the electrophilic reaction of the Advanced COPNA-Resin was not completed. In the curing process of the B-staged blends, the following phenomena were supposed to occur. Figure 9 is given to help the appreciation of the phenomena.

1. The generated benzyl-type cations attacked both π electrons of naphthalene in the B-staged Advanced COPNA-Resin and free electron pairs of nitrogen in the amino-groups of the nylon 6 because the COPNA-Resin reaction was advanced by electrophilic reaction.

$$HOCH_2-\langle O \rangle-CH_2OH \xrightarrow{H^+} HOCH_2-\langle O \rangle-\overset{+}{C}H_2 + H_2O \qquad (1)$$

$$HOCH_2-\langle O \rangle-\overset{+}{C}H_2 + \langle OO \rangle \xrightarrow{H^+} HOCH_2-\langle O \rangle-CH_2-\langle OO \rangle + H^+ \qquad (2)$$

$$HOCH_2-\langle O \rangle-CH_2-\langle OO \rangle + \langle OO \rangle \xrightarrow{H^+} \langle OO \rangle-CH_2-\langle O \rangle-CH_2-\langle OO \rangle \qquad (3)$$

$$+ H_2O + H^+$$

Figure 8 Reaction mechanism of the Advanced COPNA-Resin.

2. Here, priority of the electrophilic reaction of the benzyl-type cations is important. In order to decide the primary material, π-electrons of condensed aromatics or free electron-pairs of nitrogen in the amino-groups of the nylon 6, an experimental work was already done.[12] The mixture from naphthalene/1,4-benzenedimethanol/β-naphthalene sulfuric acid/nylon 6 whose fraction was 1/1.73/0.26/1 (by weight), was stirred at 110°C for 8 h. In the experiment, the viscosity of the mixture did not increase because the molecular weight of the Advanced COPNA-Resin hardly increased. The phenomenon suggested the following: generated benzyl-type cations attacked and combined with amino-groups of the nylon 6 with priority. The following discussion was carried out under the defined situation.

3. In the initial stage of the curing process, benzyl-type cations mainly attacked the free electron-pairs of nitrogen in the amino-groups and combined with them. At the end of this initial state, the following situation could be observed. In the case of the 30/70

Occurring probability : a < b
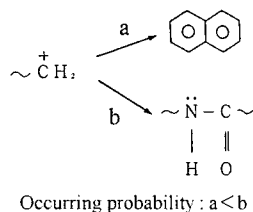
	At the 1st stage, reaction "b" proceeded. After the reaction proceeded,	At the 2nd stage, reaction "a" proceeded. After the reaction proceeded,	Domain size of the COPNA(μm)	Degree of graft reaction (%)
30/70 System (COPNA<Nylon)	a small amount of benzyl-type cations were left. (a large amount of non-reacted amino-groups were left.)	the molecular weight of the COPNA was small.	0.1~1	7.5
50/50 System (COPNA=Nylon)			1~3	42
70/30 System (COPNA>Nylon)	a large amount of benzyl-type cations were left.(a small amount of non-reacted amino-groups were left.)	the molecular weight of the COPNA was large.	>10 (poor compatibility)	82

Figure 9 Relationship between morphology and the nylon 6 fraction.

(COPNA/Nylon 6) system, a small amount of the benzyl-type cations were left, while a large amount of the secondary amino-groups were left because the COPNA fraction was much smaller than the nylon 6 fraction. In the case of the 70/30 (COPNA/Nylon 6) system, a large amount of the benzyl-type cations were left, while a small amount of the secondary amino-groups were left because the COPNA fraction was much larger than the nylon 6 fraction.

4. In the late stage of the curing process, a reaction between the benzyl-type cations and condensed aromatic rings occurred. In the case of the 30/70 system, the molecular weight of the Advanced COPNA-Resin did not increase largely because only a small amount of the benzyl-type cations were left in the system. Therefore, the domain size of the Advanced COPNA-Resin was as small as 0.1 to 1 μm, as shown in Figure 2(a). In the case of the 70/30 system, the molecular weight of the Advanced COPNA-Resin increased largely because a large amount of the cations were left in the system. Therefore, the morphology of the 70/30 system exhibited a poor compatibility, as shown in Figure 2(c).

The degree of the graft reaction was calculated from the absorbance ratio of N—H out-of-plane vibration/C=O stretching vibration. From the previous discussion, degree of consumption of the secondary amino-groups strongly depended on the nylon fraction; therefore, the degrees of the graft reaction as shown in Table II were quite different from each other in the fully-cured blend systems.

CONCLUSION

The interfacial behavior between the Advanced COPNA-Resin and the nylon 6 was studied by the spectral analyses of ^{13}C FT-NMR, ^{15}N FT-NMR, and FT-IR. It was revealed that a graft reaction occurred at the interface between the Advanced COPNA-Resin and the nylon 6. The degree of the graft reaction increased according to the decrease of the nylon 6 fraction. The relationship between the morphology and the nylon fraction of the fully-cured polymer blends was also discussed. In the discussion, the following explanation was given in order to appreciate the relationship. In the initial stage of the curing process, the generated cations mainly attacked the free electron-pairs of nitrogen in the amino-groups of the nylon 6. In the late stage, the cations left attacked the π electrons of the condensed aromatics.

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